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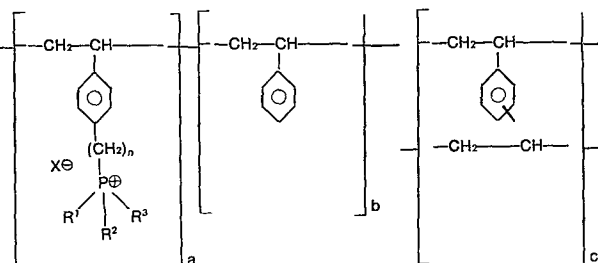
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(54) **Process for preparing primary alkyl chlorides.**

(57) In a process for the conversion of primary alkyl alcohols to the corresponding alkyl chlorides in the presence of aqueous hydrochloric acid, a catalyst, consisting of an organic resin bound or triphase catalyst prepared from lightly crosslinked polystyrene resins containing pendant halogen functionality by a quarternization reaction with tertiary phosphine with the structural formula:



[wherein the a, b, c ratio may vary between 1/98/1 to 99/0/1,

wherein R¹, R², R³ are radicals selected from the group comprised of alkyls of 1 to 12 carbon atoms, secondary alkyls of 3 to 12 carbon atoms, cycloalkyls of 5 to 8 carbon atoms, X[⊖] is a radical selected from

F[⊖], Br[⊖], Cl[⊖]

or HSO₄[⊖], and wherein n equals 1 to 12], is used.

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PROCESS FOR PREPARING PRIMARY ALKYL CHLORIDES

This is a continuation-in-part of Application Serial Number 099307, filed December 3, 1979.

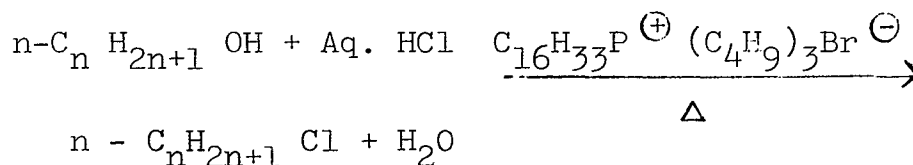
Technical Field

5 Primary alkyl alcohols can be converted to the corresponding alkyl chlorides in the presence of aqueous hydrochloric acid and a quaternary phosphonium salt, the improvement characterized in that an organic resin bound
10 or triphase quaternary phosphonium salt is used as the catalyst.

Background Art

The classical conversion of primary alcohols to alkyl chlorides requires the use of hydrogen chloride gas and the
15 presence of catalytic amounts of zinc chloride. See M.T. Atwood, Journal of American Oil Chemistry Society, 40, 65 (1963) and R. Stroh, W. Hahn and Houben-Weyl, Methoden der Organischen Chemie, 4th ed. E. Muller, Ed., Vol. V/3, Georg Thieme Verlag Stuttgart, 1962, p. 831. The references
20 disclose that use of aqueous hydrochloric acid is less suitable since anhydrous reaction conditions are preferred. These methods give poor yields and require the use of a large amount of zinc chloride. See A. Guyer, A. Bieler, and E. Hardmeyer, Helv. Chim. Acta 20, 1463 (1937).

25 Landini, Montanari and Rolla in Synthesis, January 1974, page 37 reported that the problems of poor yield and excessive amounts of reactants can be overcome when the reaction is carried out in the presence of a phase-transfer catalyst in a heterogenous system. The following equation
30 is indicative of Landini et al's reaction:



35

Prior to the advent of the phase-transfer catalyst concept the general order of reactivity of alkyl halides was normally $RI > RBr > RCl$. Unfortunately this order of reactivity is just the reverse of their economic desirability. This fact has led to the very limited industrial applications of alkyl halides.

Recently using the phase-transfer concept it has been discovered that the order of reactivity of the alkyl halides is $RCl > RBr > RI$ in some cases.

It has been reported that when water insoluble primary alcohols are reacted with aqueous concentrated hydrochloric acid at $105^{\circ}C$. in the presence of catalytic quantities of hexadecyltributylphosphonium bromide, the conversion into corresponding primary alkyl chlorides averaged 60% after 8 hours and reached 90 and 95% after 30 and 45 hours respectively. Landini et al, Synthesis, page 37, supra, determined that the chain length of the primary alkyl alcohol had no noticeable effect on the rate of conversion in the series of alcohols from 6 to 16 carbon atoms. It was found both yields and reaction rates drastically dropped in the case of water-soluble alcohols. Additionally, it was determined that the reaction proceeded without the synthesis of the undesired by-products of dialkyl ethers or isomeric chlorides.

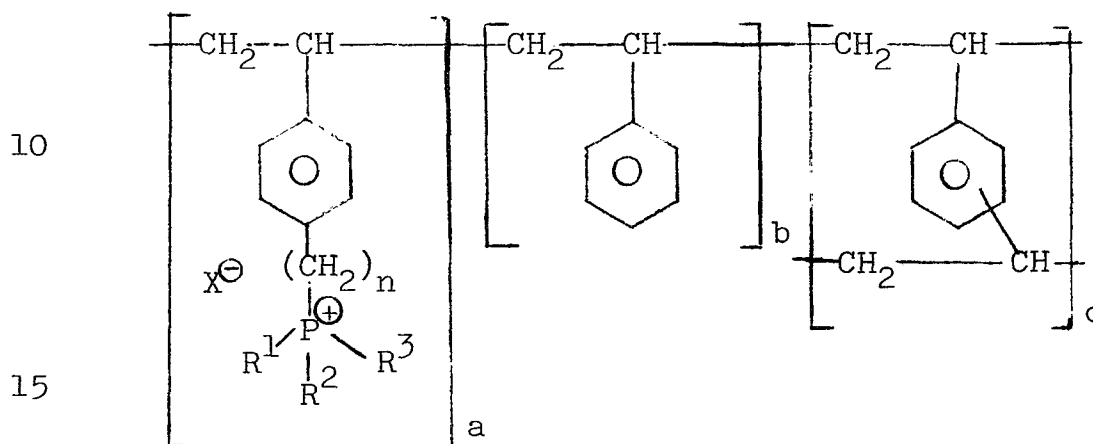
The process of the present invention unlike some cited references does not require the use of anhydrous HCl gas. By use of the process of this invention high yields of the primary alkyl chlorides can be obtained by using aqueous concentrated hydrochloric acid. The crude alkyl chlorides then may be used directly to prepare many valuable products, for example, sulfides, disulfides, esters, ethers, nitriles and etc. Industrial production of alkyl chlorides would preferably be conducted on a continuous basis due to economic benefits over batch preparations.

Disclosure of Invention

In a process for the conversion of primary alkyl alcohols

which have limited water solubility in the corresponding alkyl chlorides in the presence of

aqueous hydrochloric acid and a catalyst, the improvement characterized in that an organic resin bound or triphase catalyst prepared from lightly crosslinked (1 or 2% cross-link density) polystyrene resin containing pendant halogen functionality by a quaternization reaction with a tertiary phosphine as illustrated by the structural formula:



wherein the a, b, c ratio may vary between 1/98/1 to 99/0/1, the more preferred range being 1/98/1 to 65/34/1 with the most preferred range 5/94/1 to 30/69/1, and wherein R^1 , R^2 and R^3 are the same or different radicals selected from the group comprised of alkyls of 1 to 12 carbon atoms, secondary alkyls of 3 to 12 carbon atoms, cycloalkyls of 5 to 8 carbon atoms; X^\ominus is a halide radical selected from the group consisting of F^\ominus , Br^\ominus , Cl^\ominus or hydrogen sulfate ion HSO_4^\ominus , and wherein n equals 1 to 12; is used.

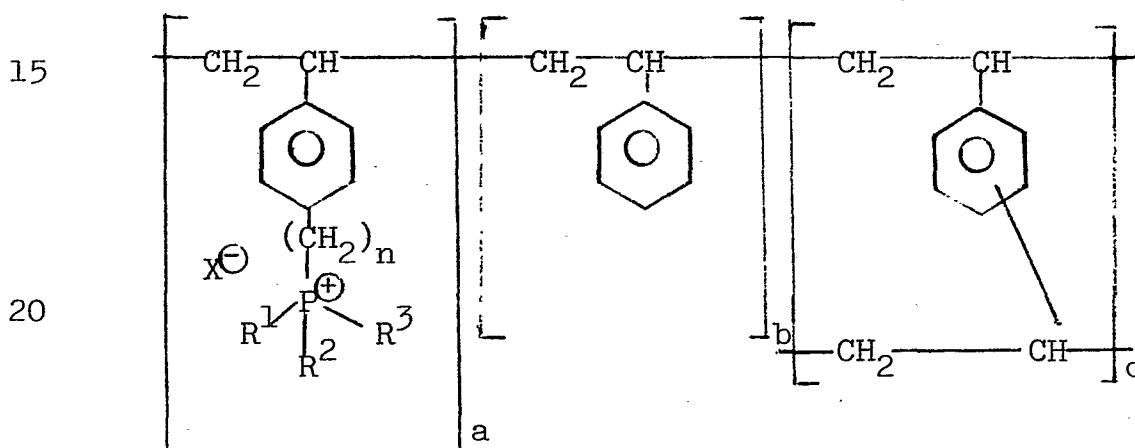
More Detailed Description of Disclosure

Representative of the alcohol starting materials used in this process are alcohols such as 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, 3-methyl-1-butanol, 3,3-dimethyl-1-butanol and 4-methyl-1-pentanol.

Representative of the products formed by the process of this invention are alkyl chlorides such as 1-chloropentane, 1-chloroheptane, 1-chlorooctane, 1-chlorononane, 1-chlorodecane, 3-methyl-1-chlorobutane, 3,3-dimethyl-1-chlorobutane and 4-methyl-1-chloropentane. The process of this invention is continuous as the alkyl chloride product is removed by distillation of the alkyl chloride azeotrope with water.

It has been determined that the phosphonium ions are somewhat more effective and thermally stable than the corresponding ammonium catalyst in the process of this invention. It has also been determined that, in general, the longer the alkyl chain length of the catalyst the greater the efficiency of the catalyst.

The process of this invention is limited to organic resin bound or the so-called "triphasic" catalyst system. These polymer-bound catalysts may be easily prepared from lightly crosslinked (1 or 2% crosslink density) polystyrene resins containing pendent halogen functionality by a quaternization reaction with a tertiary phosphine as illustrated by the following formula:



wherein the a, b, c ratio may vary between 1/98/1 to 99/0/1, the more preferred range being 1/98/1 to 65/34/1 with the most preferred range 5/94/1 to 30/69/1, and wherein R^1 , R^2 , R^3 are the same or different radicals selected from the group comprised of alkyls of 1 to 12 carbon atoms, secondary alkyls of 3 to 12 carbon atoms, cycloalkyls of 5 to 8 carbon atoms. X^\ominus is a halide radical selected from the group consisting of F^\ominus , Br^\ominus , Cl^\ominus or hydrogen sulfate ion HSO_4^\ominus , and wherein n equals 1 to 12.

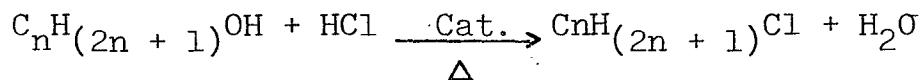
As an example, polymer bound benzyl-tri-n-butyl phosphonium chloride is prepared according to the following procedure:

A 2 liter 3 neck flask equipped with a mechanical stirrer, condenser, thermometer and nitrogen gas inlet was charged with

103 grams (0.124 moles chloride content) of chloromethylated 1% crosslinked polystyrene resin (marketed under the trade name Bio-Beads SX-1). The resin was then swollen by the addition of 1 liter dimethylformamide. The system was purged
5 with a stream of nitrogen and 32.4 grams (.160 moles) tri-n-butyl phosphine was added. The mixture was brought to 120-130°C. with stirring for four hours. The mixture was then cooled to 70°C., filtered warm and subsequently washed with dimethylformamide three times and with acetone
10 four times. The resin was dried in a vacuum oven at 80-100°C. providing the catalyst resin in a yield of 131.3 grams.

Best Mode For Carrying Out The Invention

15 The overall reaction may be represented by the following equation:



20 wherein $5 \leq n \leq 10$.

As little as 1 mol% of phosphonium salt catalyst per mole of alcohol may be used, however, due to the stability of the catalyst under the reaction conditions, it is advantageous and desirable to increase the catalyst level to 10, 20, 50
25 or more mole percent per mole of alcohol to increase the rate of conversion of alcohol of chloride. As little as 1.5 moles of concentrated 37% aqueous hydrochloric acid per mole of alcohol in the reaction vessel can be used, however, it is advantageous to use from 5 to 20 moles of aqueous hydro-
30 chloric acid per mole of alcohol to speed conversion.

Provided to illustrate, but not limit the scope of the present invention is the following example:

EXAMPLE I

Preparation of 1-Chlorohexane Using

35 Polymeric Phosphonium Catalysts

Preparation of Catalyst

To a one liter flask was added 50 grams of 1% cross-linked chloromethylated polystyrene resin containing 1.24

meq. chlorine per gram resin, 500 milliliters of dimethylformamide and 16.2 grams (0.08 moles) of tributylphosphine. The mixture was heated with stirring for four hours at 120 to 130°C. The mixture was cooled and filtered and the product was washed with dimethylformamide 3 times and then with acetone 3 times. The product was dried in a vacuum oven at 100°C. yielding 69.4 grams.

Preparation of 1-Chlorohexane

Of the phosphonium resin just prepared 32.3 grams of the phosphonium resin containing 0.08 moles phosphorus was added to 103 grams (1 mole) of n-hexyl alcohol in a 2 liter flask. 500 milliliters of concentrated hydrochloric acid and a few boiling chips were added to the mixture. A condenser was attached and the mixture refluxed for 43 hours under slow stirring. The mixture was cooled and the resin catalyst was filtered off. The organic layer was separated from the filtrate in a separation funnel yielding 54 grams of a pale yellow liquid. The resin was then washed with a mixture of water and CH_2Cl_2 as a reslurry. The lower organic layer was separated from the filtrate and the CH_2Cl_2 was distilled off using a hot water bath at approximately 50°C. There remained a residue of 59.1 grams which was shown by gas chromatography to be 1-chlorohexane. The total yield was 113.1 grams (.94 moles) or 93.7% of theory.

Industrial Applicability

The process of the present invention would greatly enhance the industrial use of alkyl chlorides since the tri-phase catalysts will greatly lessen the cost of production. In and of themselves alkyl chlorides can be used in numerous ways, however, the major value of these alkyl chlorides is their ability to be used as intermediates in the preparation of many materials.

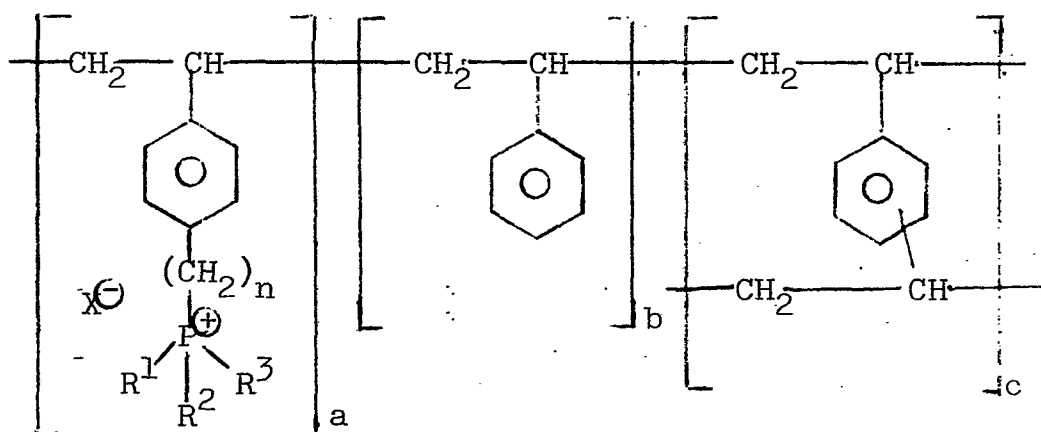
It is evident that the process of this invention would greatly enhance the productivity of alkyl chlorides in that the reaction proceeds yielding products in good yield and good purity.

5 It is believed that because of the tri-phase catalyst systems, the use of the alkylchlorides will become more widespread as industry accepts and develops this technique.

10 While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

CLAIMS

1. In a process for conversion of primary alkyl alcohols to the corresponding alkyl chlorides in the presence of aqueous hydrochloric acid and a catalyst, the improvement characterized in that an organic resin bound or triphase catalyst prepared from lightly crosslinked (1 or 2% crosslink density) polystyrene resins containing pendant halogen functionality by a quarternization reaction with tertiary phosphine as illustrated by the structural formula:



wherein the a, b, c ratio may vary between 1/98/1 to 99/0/1, the more preferred range being 1/98/1 to 65/34/1 with the most preferred range 5/94/1 to 30/69/1, and wherein R^1 , R^2 , R^3 are the same or different radicals selected from the group comprised of alkyls of 1 to 12 carbon atoms, secondary alkyls of 3 to 12 carbon atoms, cycloalkyls of 5 to 8 carbon atoms; X^- is a halide radical selected from the group consisting of F^- , Br^- , Cl^- or hydrogen sulfate ion HSO_4^- , and wherein n equals 1 to 12; is used.

2. A process according to claim 1 wherein the primary alkyl alcohol is selected from the group consisting of 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, 3-methyl-1-butanol, 3,3-dimethyl-1-butanol, 4-methyl-1-pentanol.



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EUROPEAN SEARCH REPORT

0030516

Application number

EP 80 63 0056

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A, D	SYNTHESIS, January 1974 STUTTGART (DE) D. LANDINI et al.: "Conversion of primary alcohols to alkyl chlorides using aqueous hydrochloric acid in the presence of phase-transfer catalysts" pages 37-38 --	1	C 07 C 19/02 17/16 B 01 J 31/06 //C 08 F 8/40
A	<u>US - A - 3 708 462</u> (S.V. McKINLEY et al.) * abstract * -----		TECHNICAL FIELDS SEARCHED (Int. Cl. ³) C 07 C 17/16 19/02 B 01 J 31/06 31/08 C 08 F 8/40
			CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons &: member of the same patent family, corresponding document
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 26-02-1981	Examiner VAN GEYT